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CORROSION AND PASSIVATION OF HIGH TEMPERATURE SUPERCONDUCTORS

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December 20, 1992

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## PART I.

### a. *Papers Submitted to Referred Journals*

1. Reactions  $\text{Yb}_2\text{Cu}_3\text{O}_{6.5+x}$  in Gaseous and Liquid Environments, Krystyna Brzezinska and Stanley Bruckenstein, Journal of Superconductivity, Submitted.
2. Electroless and Electro-Deposition of Silver and Copper on  $\text{Yb}_2\text{Cu}_3\text{O}_7$ , Krystyna Brzezinska, Stanley Bruckenstein, Mark V. Parish and M. J. Neal, J. Appl. Electrochem., Submitted.

### b. *Papers Published or in Press in Refereed Journals*

1. Determination of the Oxygen Content in  $\text{Yb}_2\text{Cu}_3\text{O}_{6.5+x}$ , Stanley Bruckenstein and Peter K. Wrona, Anal. Chim. Acta, 237, 421-428 (1990).
2. Effect of Carbon Dioxide on the Reaction of  $\text{Yb}_2\text{Cu}_3\text{O}_{6.5+x}$  with Water Vapor, Krystyna Brzezinska, Stanley Bruckenstein, Lori Jo Klemptner and James D. Hodge, J. Mat. Sci., In Press.

### c. *Books (and sections thereof) Submitted for Publication.*

None

### d. *Books (and sections thereof) Published.*

None

### e. *Technical Reports Published and Papers Published in Non-Referred Journals.*

1. Stanley Bruckenstein, Chairman of Workshop No. 2 and author of Workshop Report "Environmental and thermal stability of the 1-2-3 material and phase equilibria of HTSC materials." HTSC Program Conference, DARPA. September 13-15, 1988. Arlington, VA.

### f. *Patents Filed*

None

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None

### h. *Invited Presentations at Topical or Scientific/Technical Conferences.*

1. Stanley Bruckenstein. "Investigating the Corrosion and Passivation of HT Superconductors." DARPA Kickoff HTc Conference. Washington DC. September 1988 (ONR)
2. Stanley Bruckenstein. "Approaches to Investigating the Corrosion and Passivation of HT Superconductors." American Chemical Society. Los Angeles, California. September 1988. (ONR)
3. Stanley Bruckenstein. "In Situ Applications of the Quartz Crystal Microbalance. 19th International Symposium on Analytical Chemistry." Sponsored by Microbalance. U.S. Environmental Protection Agency, University of Georgia, International Association of Environmental Analytical Chemistry and

ACS Division of Analytical Chemistry and Division of Environmental Chemistry. Jekyll Island, Georgia. May 24, 1988. (ONR)

4. Stanley Bruckenstein. "HTc Research at SUNY/Buffalo". CPS Superconductor Corporation, Milford, Mass. June 13, 1989. (ONR)

5. Stanley Bruckenstein. "Reaction of  $\text{Yb}_2\text{Cu}_3\text{O}_7$  with Water Vapor and  $\text{CO}_2$ ". Northeast Regional Meeting of the ACS, Potsdam, NY. June 17, 1990 (ONR)

- h. *Contributed Presentations at Topical or Scientific/Technical Conferences.*

Stanley Bruckenstein, Participant in Session dealing with "Analytical Methods for Characterizing HTSC Powders". High Temperature Superconductors Workshop, DARPA, April 17-18, 1989. Herndon, Va. (Helped specify analytical sensitivity and accuracy for a variety of optical spectroscopic and chemical techniques.) (ONR)

- j. *Honors/Awards Prizes.*

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- k. *Number of Graduate Students Receiving Full or Partial Support on ONR Contract.*

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d. **Brief Description of Project**

Metal oxide superconductors such as  $\text{Y}_3\text{Ba}_2\text{Cu}_3\text{O}_7$  exhibit superconductivity above 90 K. These materials are chemically reactive and their reaction products will not be superconductive. The object of this research is to study the reactions of the yttrium-barium-copper superconductor with species to which it may be exposed. This exposure may occur just after synthesis, during storage before fabrication into a device, during the fabrication process, during storage and transportation of the fabricated device, and during operation as a superconducting device. Chemical investigations will involve gas and solution phase reactivity studies. Products of the corrosion process will be identified by electrochemistry, microgravimetry, various surface analysis techniques, and classical chemical analysis. The mechanisms of the corrosion processes will be determined for the purpose of identifying ways to prevent corrosion. The superconductor will then be treated with a variety of passivating materials to prevent these corrosion reactions. The mechanism of the passivation process will be studied in order to provide a basis for selecting encapsulating materials and discovering passivators.

e. **Abstract of Significant Results**

Silver and copper were deposited by electroless deposition upon  $\text{YBa}_2\text{Cu}_3\text{O}_7$  (bulk pieces and fibers). The electrical properties of these coated materials were determined by the four-point resistivity method. Good electrical contact between electroless silver layers and the  $\text{YBa}_2\text{Cu}_3\text{O}_7$  substrate could be attained. Copper was electrodeposited on electroless silver layer provided excellent environment protection to the underlying  $\text{YBa}_2\text{Cu}_3\text{O}_7$ .

The stability of  $\text{YBa}_2\text{Cu}_3\text{O}_{6.5+x}$  powder in various aqueous and nonaqueous environments was studied. The time dependence of sample weight and oxygen content,  $x$ , were determined for the samples exposed to atmospheres saturated with concentrated ammonium hydroxide, glacial acetic acid, acetone, hexane, toluene, ethanol and methanol. Little evidence for reaction was found for the latter five organic vapors, while substantial reaction was found for the first two vapors.  $\text{YBa}_2\text{Cu}_3\text{O}_{6.5+x}$  powder was also suspended in deionized water and aqueous 1 molar solutions of NaCl, KCl,  $\text{KNO}_3$ , and NaBr. The results suggest that reaction is minimal and probably involves only the surface of the powder.

The influence of carbon dioxide on the reaction between  $\text{YBa}_2\text{Cu}_3\text{O}_{6.5+x}$  powder and air saturated with water vapor was studied. Superconductor powder samples were exposed to air that was saturated with water vapor which a) was free of  $\text{CO}_2$ , b) was saturated with  $\text{CO}_2$ , and c) contained ambient level  $\text{CO}_2$ . In another experiment, the effect of pure, dry  $\text{CO}_2$  (1 atmosphere partial pressure) was studied. The time variations of sample weight, oxygen content and XRD spectrum were determined. In water-saturated air, the rate of decrease of oxygen content in  $\text{YBa}_2\text{Cu}_3\text{O}_{6.5+x}$  decreased with increasing partial pressure of  $\text{CO}_2$ . X-Ray diffraction was used to identify the reaction products. Higher partial pressures of  $\text{CO}_2$  favor the formation of

a barrier layer ( $\text{BaCO}_3$ ) which inhibits the reaction of the underlying  $\text{YBa}_2\text{Cu}_3\text{O}_{6.5+x}$  with water vapor. Very little decrease in oxygen content occurred on exposure of  $\text{YBa}_2\text{Cu}_3\text{O}_{6.5+x}$  to pure, dry  $\text{CO}_2$ .

A new method for determining the oxygen content of the high temperature superconductor,  $\text{YBa}_2\text{Cu}_3\text{O}_{6.5+x}$ , is described. The superconductor is dissolved in 4.4 M hydrobromic acid, forming bromine. The mixture is then diluted with hydrochloric acid to obtain a solution of bromine and cupric ion in 0.44 M hydrobromic acid and 1.1 M hydrochloric acid. As(III) is added in slight excess of that required to react with the bromine, and the unreacted As(III) is determined by titration with potassium bromate. Oxygen does not interfere. The results of this method are in agreement with other iodometric procedures. The dissolution of the superconductor in 4.4 M hydrobromic acid is much faster than in hydrochloric acid, the medium used in one iodometric technique. This method was used to analyze  $\text{YBa}_2\text{Cu}_3\text{O}_{6.5+x}$  sintered fibers and powder samples weighing from ca. 0.5 mg to 200 mg for oxygen content.

## PART III

### III.A. Aqueous Deposition of Metals on $\text{YBa}_2\text{Cu}_3\text{O}_7$

#### III.A.1. Introduction

The coating of the high temperature superconductor  $\text{YBa}_2\text{Cu}_3\text{O}_7$  (YBaCuO) with a impermeable, highly conducting barrier layer is necessary. Such a barrier coating would protect the reactive YBaCuO from degradation by reaction with its environment (e.g., moist air) during storage and fabrication into a device. It would also provide a low resistance shunt path for the current in the event that a region were to go "normal". Coating YBaCuO objects with metals immediately comes to mind.

Rosamilia and Miller reported that they could not electrodeposit copper on YBaCuO from a variety of aqueous supporting electrolytes, while silver and mercury could be deposited[1]. YBaCuO reacts with aqueous supporting electrolytes readily, and depending upon the acidity, the anion present and potential, may dissolve freely or selectively [2] [3]. Later Rosamilia and Miller showed that silver, copper, lead and tin can be successfully deposited from several nonaqueous solvents [4][5]. They also reported that certain superconducting oxide materials can be conveniently electroplated from selected electrolytes in either nonaqueous or aqueous solvents<sup>5</sup>. A number of metals can be plated: silver, copper, tin, lead and tin-lead alloys.

Reich and Felner prepared a non-random silver-YBaCuO composite[6]. An electroless deposition process was used by them to coat YBaCuO particles with silver, and these coated particles were then sintered (400 - 900 C) to form a superconducting composite. The measurement of the transport and magnetic properties of these composites showed that they exhibit higher critical currents than pure, bulk YBaCuO. Also, the "materials exhibit hardness properties similar to those of ductile metals."

Rubin et. al. studied the electrical and magnetic properties of silver, copper and lead deposited from acetonitrile onto YBaCuO[7]. They found that there was no degradation of the bulk properties of YBaCuO and that the contact resistance between silver and the superconductor was similar to that found with ultrasonically soldered indium.

The electrodeposition of copper and silver from aqueous solution has been reported by Kaneto and Yoshino[8]. Presumably the deposition of copper by the latter authors as compared to the results of Rosamilia and Miller<sup>1</sup> is related to the difference in cupric ion concentrations employed by these two groups.

In this work we comment on various aspects of copper and silver electro(less) deposition from aqueous solution onto bulk YBaCuO and YBaCuO fibers. We also report the resistance/temperature behavior of such electrolessly coated fibers.

#### III.A.2. Results and Discussion

All YBaCuO fibers had dimensions in the range 100 to 200  $\mu$ . Electron microscopy was used to assess fiber and deposited metal film dimensions.

*III.A.2.1. Electrodeposition of Copper and Silver.* We initially investigated the aqueous electrodeposition of copper and silver upon YBaCuO fibers. Using a conventional acid-copper bath (current density =  $0.04 \text{ A cm}^{-2}$  for 20 minutes) no deposit of copper was seen. If the same copper bath without acid was used (current density



0.04 A cm<sup>-2</sup>, for 20 minutes) a nonuniform coating of copper was visible, as were patches of the underlying superconductor. The failure to deposit copper from the acid bath is consistent with the free dissolution of YBaCuO at the most cathodic potential sustainable in acid medium. The observations accompanying the deposition of copper from the neutral bath suggests that the copper plating process competes with the formation of an insulating layer that forms by chemical reaction with the plating solution.

Silver electrodeposition (current density 0.001 A cm<sup>-2</sup> for 69 minutes) occurred, yielding a nonuniform coating that grew slowly. Again, the nonuniform growth pattern suggested that an insulating layer formed by reaction with the YBaCuO and the plating solution during the plating process.

It should be noted that the fibers used in these experiments are small in diameter and are fragile and that no mechanical treatment to remove pre-existing surface films, if any, was possible.

*III.A.2.2. Electroless Silver Deposition.* The electroless silver-coated fibers appeared smooth and were uniformly coated. The silver layer is about 3-4 μm thick. After electroless silver deposition, a fiber yielded a  $J_c$  of about 1400 A cm<sup>-2</sup>, as seen in Figure A.1.  $T_c$  was determined after electroless deposition and the result is shown in Figure A.2 (open squares). Both these  $J_c$  and  $T_c$  results are typical of an untreated fiber. These results confirm that the electroless deposition process does not necessarily degrade the bulk of the fiber (by chemical reaction after some infiltration mechanism). The resistance in the vicinity of  $T_c$  is about 0.35 μohm-cm, which is non-zero below  $T_c$ ; a fiber that has not been treated has  $\rho = 0$ .  $T_c$  and the value of the specific resistance was redetermined after a subsequent thermal/oxygen annealing the fiber (solid squares). Annealing this fiber decreased the specific resistance effectively to 0 μohm - cm within the measurement error. Oxygen annealing can frequently, but not always, decrease the resistance of a fiber as compared to its value before annealing. See Figure A.3 for the specific resistance vs temperature plot for another annealed fiber.

*III.A.2.3. Electroless Silver Deposition + Copper Electrodeposition.* A YBaCuO fiber was coated with electroless silver and then a layer of copper was electrodeposited from the acid copper bath using a current density of 0.03 A cm<sup>-2</sup> for 7 minutes. The thickness of the silver coating is 7-8 μm and that of overlayer of copper is 2-3 μm. There was a region of porosity down the center of this fiber. The YBaCuO near that hole was not distinguishably different from the bulk YBaCuO, or the YBaCuO near the metal overlayer. Figure A.4 shows the resistance-temperature curve. A superconducting transition is seen at about 90 K, and the resistance falls to about 1 μohm-cm indicating that the current path is partially through the silver coating. This suggests, but does not confirm, the presence of a barrier layer between the metal and superconductor.

*III.A.2.4. Environmental Protection by Copper Coating.* Four bulk YBaCuO samples ( $d = 5.6136$  g/cm<sup>3</sup>) were initially coated with electroless copper. They were then electrolytically plated with copper using the neutral copper sulfate bath for 0.5 hour at a current density of about 1.8 A/dm<sup>2</sup>. These samples were dried, weighed, and then submerged in 0.1 M sulfuric acid for 3 hours, washed with water. The samples were then dried and weighed again. The initial weights and weights after three hours sulfuric acid treatment for these four samples were: Sample 1= 1.2230 g and 1.2222 g; sample 2= 0.8150 g and 0.8147 g; sample 3= 0.7072 g and 0.7070 g; and sample 4= 0.8814 g and 0.8812 g. No significant weight change occurs under these highly corrosive conditions in which an unprotected fragment of YBaCuO would completely dissolve in less than one hour.

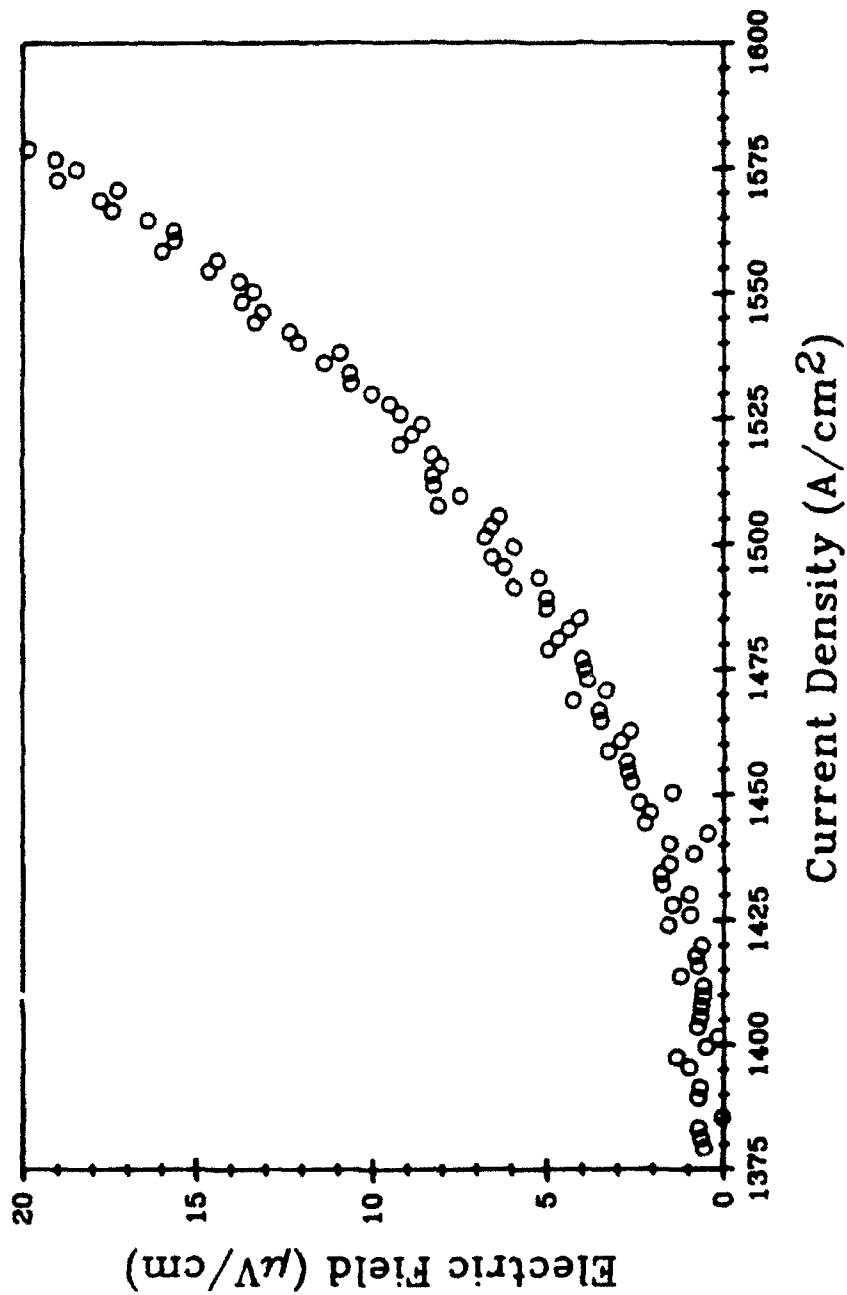


Figure A.1. Effect of electric field on current density at 77 K for typical fiber after electroless silver deposition.  $J_c$  about  $1400 \text{ A cm}^{-2}$  @ self field.

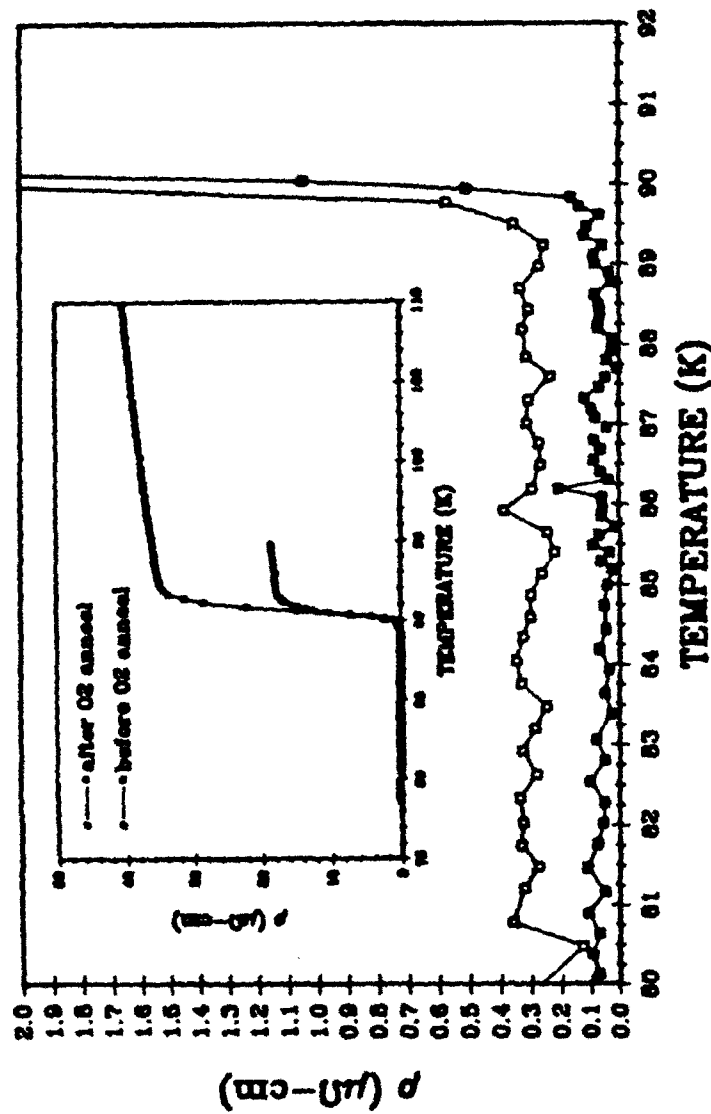


Figure A.2. Specific resistance vs temperature for an electroless silver coated fiber. Open squares— before thermal/oxygen annealing; closed squares— after thermal oxygen annealing a furnace under flowing oxygen. The furnace temperature was ramped to 850 °C, and then, without any holding time, it was cooled to 520 °C in 2 hours where this temperature was maintained for 8 hours. The furnace was then cooled to room temperature. The fiber was silver-coated by two immersions of ten minutes in the electroless bath, followed by electrolysis in an acid copper bath for 7 minutes using a current density of 0.03 A cm<sup>-2</sup>.

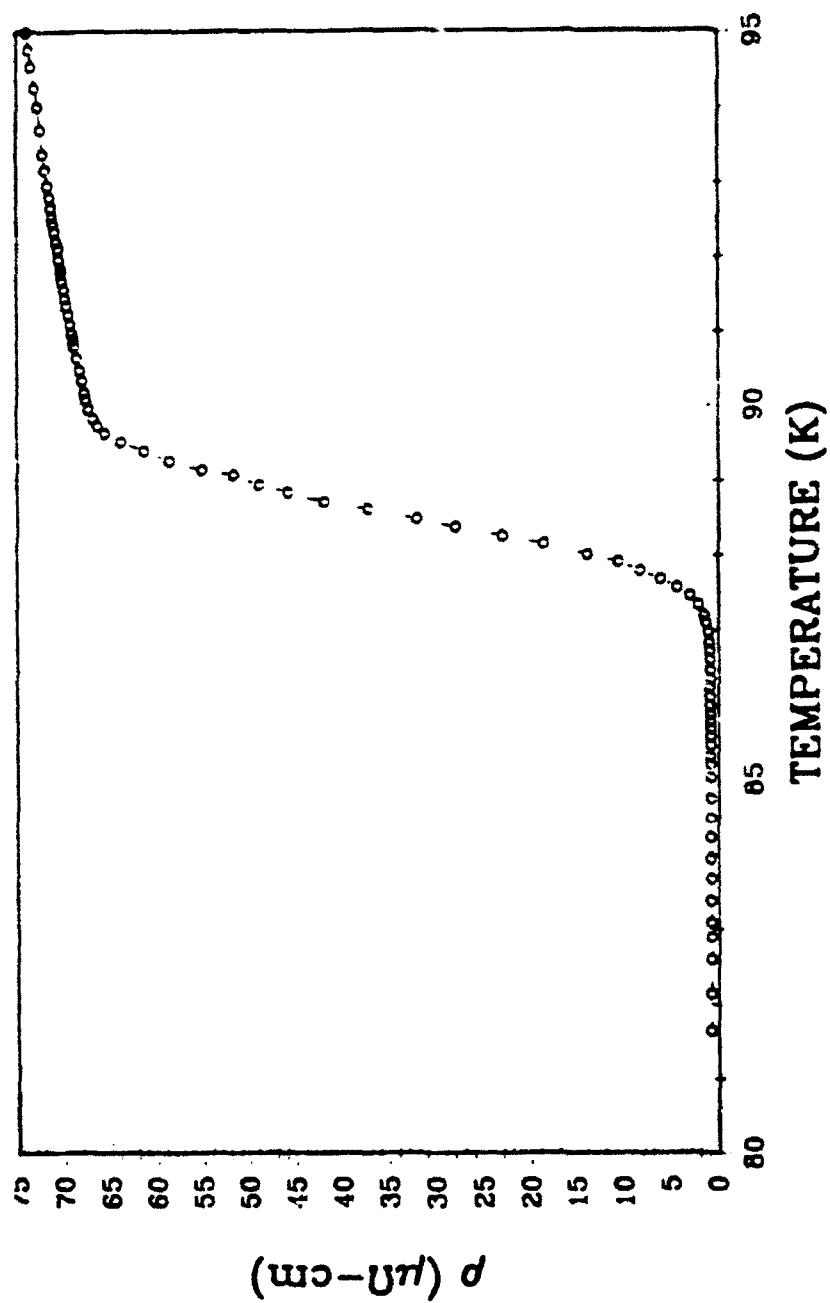


Figure A.3. Specific resistance vs temperature for another YBaCuO fiber prepared analogously to the fiber of Figure A.2 and oxygen annealed.

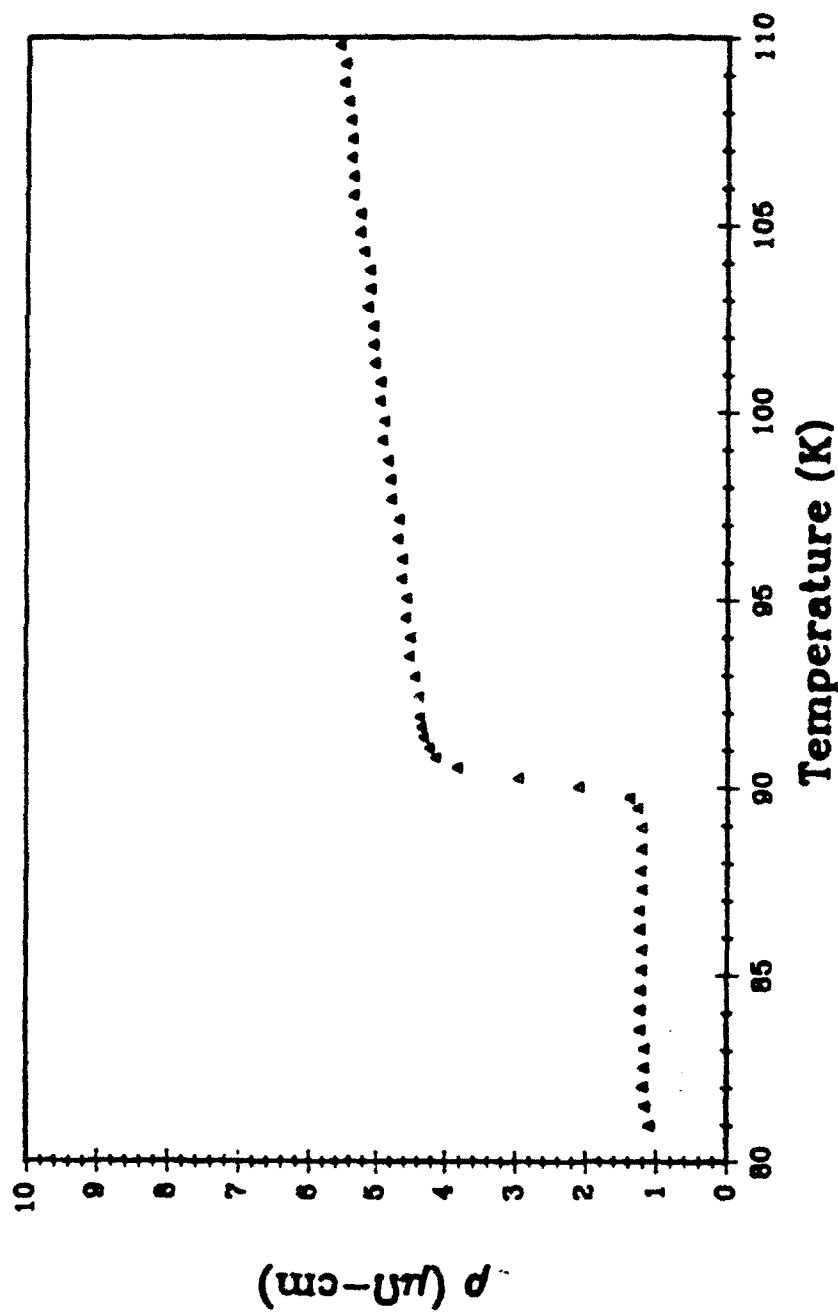


Figure A.4. Specific resistance vs temperature for a YBaCuO fiber. The fiber was silver-coated by two immersions of ten minutes in the electroless bath, followed by electrolysis in an acid copper bath for 7 minutes using a current density of  $0.03 \text{ A cm}^{-2}$ .

### III.A.3. Conclusions

Electroless deposition of copper and silver from aqueous solution onto YBaCuO is possible. Good electrical contacts between YBaCuO and electroless silver are obtained. The electroless silver technique could readily be used to form silver contacts on YBaCuO surface regions by placing a few drops of the electroless bath on the surface and waiting a few minutes for the deposition process to occur. Copper can be electrodeposited on the electroless silver layer. Copper layers formed by electrodeposition onto electroless copper provide excellent environment protection to the underlying YBaCuO.

### III.A.4. Acknowledgement

This work at Buffalo was aided by the CPS Superconductor Corporation by Defense Advanced Research Projects Agency Contract # N 00014-88-C-0512. The assistance of Dr. V.M. Pathare in performing the electron microscopy studies required in this work is acknowledged.

### III.A.5. Literature.

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### III.B. Reactions $\text{YBa}_2\text{Cu}_3\text{O}_{6.5+x}$ in gaseous and liquid environments

#### III.B.1. Introduction

Shortly after the discovery<sup>1</sup> of superconductors with transition temperatures  $> 90$  K, e.g.  $\text{YBa}_2\text{Cu}_3\text{O}_{6.5+x}$ , it was observed that they were very chemically reactive, and would decompose rapidly on exposure to water, water vapor and humid air<sup>2-14</sup>. Information concerning the reactivity of superconducting perovskites is important, but limited<sup>4,10,11,12,15,16</sup>.

The stability of  $\text{YBa}_2\text{Cu}_3\text{O}_{6.5+x}$  in contact with various liquids, mainly alcohols and aqueous alkaline media was studied by Barns and Laudise<sup>4</sup>.  $\text{YBa}_2\text{Cu}_3\text{O}_{6.5+x}$  reacts much faster in aqueous acid media as compared to basic solution in which the rate is quite slow; but in strongly basic solutions at higher temperatures the rate of reaction becomes significant. In methanol,  $\text{YBa}_2\text{Cu}_3\text{O}_{6.5+x}$  is stable at room temperature, but decomposes relatively rapidly at higher temperatures even under basic conditions.

Trolier et al.<sup>12</sup> studied the dissolution of  $\text{YBa}_2\text{Cu}_3\text{O}_{6.5+x}$  in a number of organic liquids, and found little dissolution occurred by 220 hour exposure to benzene, toluene, acetone, methanol, isopropanol or dimethylformamide. Any small dissolution that did take place was incongruent.

McDevitt et al.<sup>15</sup> investigated the chemical and electrochemical stability of  $\text{YBa}_2\text{Cu}_3\text{O}_{6.5+x}$  electrodes in various environments at temperatures above  $T_c$ .  $\text{YBa}_2\text{Cu}_3\text{O}_{6.5+x}$  was found to be stable in dry aprotic solvents such as acetonitrile for extended periods of time. As reported previously<sup>10</sup>, they found that  $\text{YBa}_2\text{Cu}_3\text{O}_{6.5+x}$  reacts more rapidly in aqueous acid solutions than in basic ones.

Bachtler et al.<sup>16</sup> described the behavior of  $\text{YBa}_2\text{Cu}_3\text{O}_{6.5+x}$  electrodes in aqueous solutions. The best surface stability was found in alkaline solutions. The dissolution rate of copper oxide is low in alkaline media, virtually negligible. The surface composition and structure depended on the time of contact with the aqueous electrolyte.

High area powders are the precursors from which bulk devices will be fabricated, and control of the quality of these starting materials is critical. Where reaction is possible, such high area powders can be expected to show very rapid corrosion rates. Our approach takes advantage of the intrinsically larger rates of reaction of high area powders as compared to bulk forms of a solid and is based on the chemical determination of the x-value and weight change after controlled exposure of the powder to a number of gaseous phases and both aqueous and nonaqueous liquids. These environments were chosen to highlight a specific possible class of chemical reactions.

#### III.B. 2. Experimental procedure.

*III.B. 2. Reaction with Aqueous Electrolyte Solutions.* About 0.2 g of oxygenated  $\text{YBa}_2\text{Cu}_3\text{O}_{6.5+x}$  powder was added to a flask containing 20 ml of one of the following solutions: deionized water, 1M KCl, 1M  $\text{KNO}_3$ , 1M NaBr and 1M NaCl which had been purged with nitrogen for 15 minutes. The flask containing the suspension of  $\text{YBa}_2\text{Cu}_3\text{O}_{6.5+x}$  and solution was tightly stoppered, placed in an ultrasonic bath for either 10 minutes or 30 minutes. The iodometric titration method was used to determine the oxygen content of  $\text{YBa}_2\text{Cu}_3\text{O}_{6.5+x}$  samples before and after treatment with a given aqueous solution. This was done in two stages. First, the suspension of  $\text{YBa}_2\text{Cu}_3\text{O}_{6.5+x}$  powder and aqueous solution was analyzed for total iodine-producing species using the same iodometric method. In the first method, the total contents of the flask were analyzed by adding 80 ml of oxygen-

free 0.4 M HCl containing 7.76g of KI was added to the flask to dissolve the  $\text{YBa}_2\text{Cu}_3\text{O}_{6.5+x}$ . The iodine which formed was titrated with standard 0.1002M sodium thiosulfate using starch (4 ml of 0.2%) as the indicator. The value of X was calculated using the standard procedure <sup>14</sup>. In the second method, the contents of the flask after the ultrasonication treatment were filtered using Fisher brand Q2 filter paper and the filter paper and the filtrate collected. The solid in the filter paper was then washed with 5 ml of deionized water which was pooled with the original filtrate. The total filtrate was then mixed with 80 ml of oxygen-free 0.41M HCl containing 7.76g of KI and the iodine which formed was titrated with standard 0.0100M sodium thiosulfate adding 4 ml of 0.2% starch solution just before the endpoint. A second filtrate prepared as described above was mixed with 80 ml of nitrogen purged 0.41 M HCl and the solution allowed to stand for 30 minutes. Then 7.76g of potassium iodide was added the iodine produced titrated with sodium thiosulfate. The value of x was calculated from the equation:

$$x = 1.5 (V_1 - V_2)/V_2 \quad (1)$$

where  $V_1$  is the volume of titrant per gram of  $\text{YBa}_2\text{Cu}_3\text{O}_{6.5+x}$  required to reach the endpoint of the first titration and  $V_2$  in the corresponding value for the second titration.

*III.B. 2.2. Reaction with Vapors.* The samples, c.a. 0.2 g, were weighed onto watchglasses which were then placed in a desiccator containing of one of the following solutions: concentrated ammonium hydroxide, glacial acetic acid, ethanol (anhydrous), methanol (anhydrous), n-hexane (99 mol % pure), toluene and acetone. The  $\text{YBa}_2\text{Cu}_3\text{O}_{6.5+x}$  samples were exposed to these atmospheres for a measured amount of time in the range from 1 hour to 72 hours. After exposure the samples were weighed and placed in a desiccator containing solid NaOH or concentrated sulfuric acid. The samples remained until constant weight was achieved (24 to 36 hours). The oxygen content ( $6.5 + x$ ) was determined by iodometric method before and after exposure to a vapor.

### III.B.3, Results and Discussion

*III.B.3.1 Vapor-phase reactions.* The results of reacting  $\text{YBa}_2\text{Cu}_3\text{O}_{6.5+x}$  powder exposed to vapors of concentrated ammonium hydroxide or glacial acetic acid are shown in Figures B.1 (weight increases) and B.2 (x-value decreases). The samples exposed to concentrated  $\text{NH}_4\text{OH}$  gained 15.2% after exposure for 24 hours. The samples exposed to glacial acetic acid gained 60.1% after only four hours. These samples changed from a black to blue in color; the blue color was obvious after 4 hours. It is interesting that while the mass of the sample increased much after contact with the vapors, the x-value decreased much slower (Figure B.2). This result suggests that the products of the reaction between  $\text{YBa}_2\text{Cu}_3\text{O}_{6.5+x}$  and acetic acid vapors can oxidize iodide to iodine during the analytical procedure used to determine the x-value.

The  $\text{YBa}_2\text{Cu}_3\text{O}_{6.5+x}$  samples were exposed also to the following organic vapors for 48 or 72 hours: acetone, hexane, toluene, ethanol and methanol. The results obtained with this experiment are presented in Table III.B.1. The samples exposed to the acetone, toluene, and methanol vapors exhibited no x-value changes within experimental error.



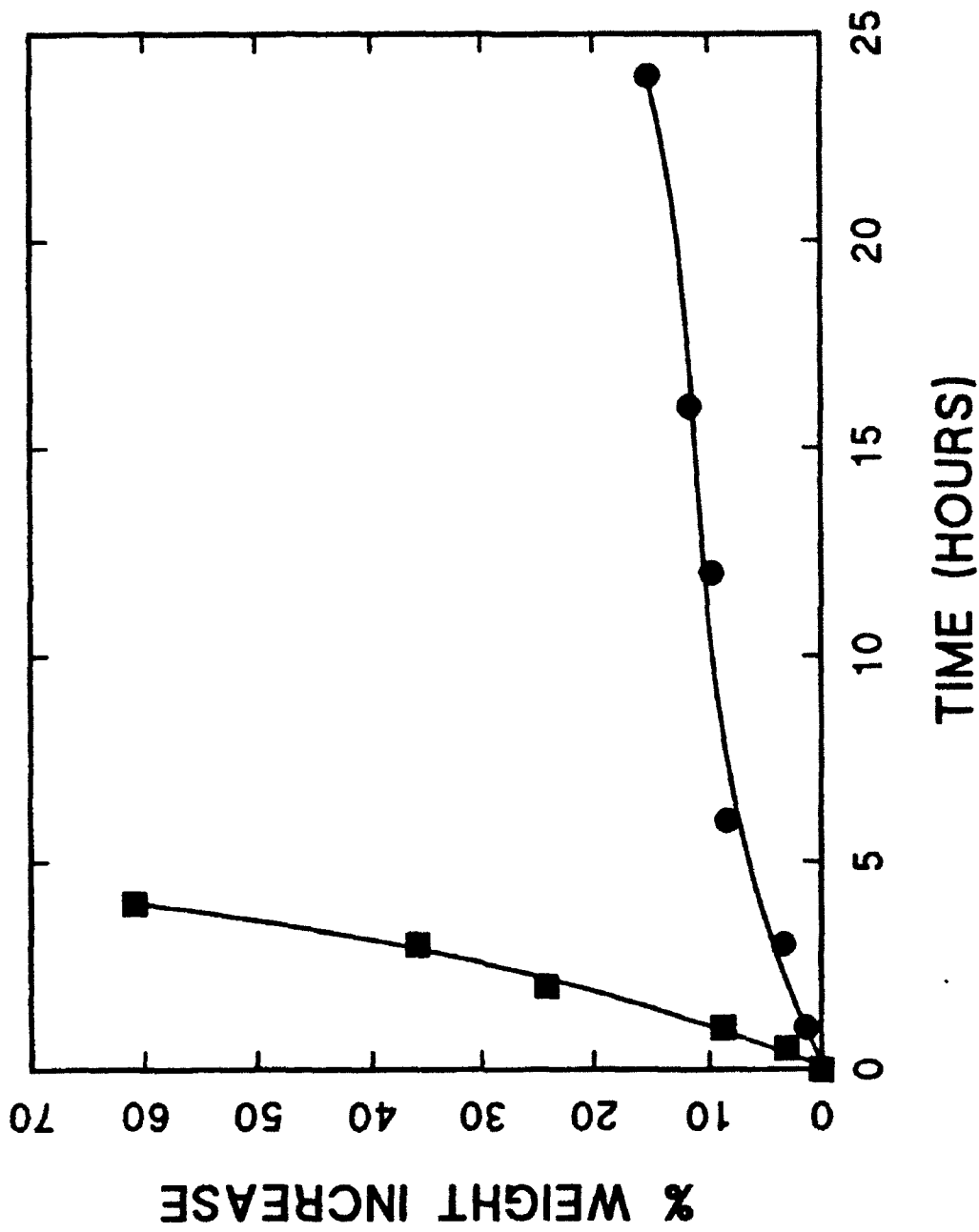


Figure B.1. % weight increase vs. time. The samples were exposed to: ●— concentrated ammonium hydroxide vapors, ■— glacial acetic acid vapors.

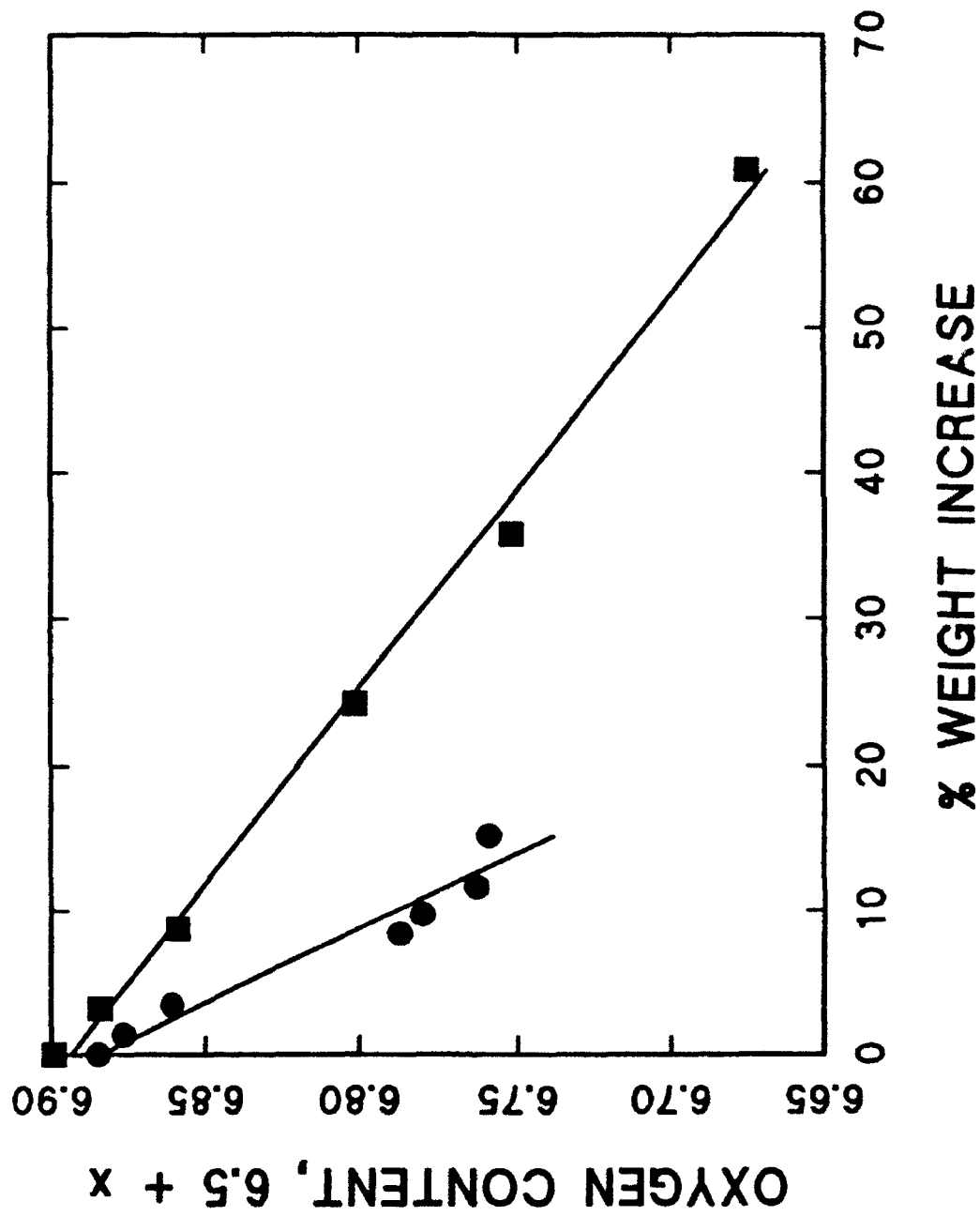


Figure B.2. Effect of sample weight gain and oxygen decrease. The samples were exposed to: ●— concentrated ammonium hydroxide vapors, ■— glacial acetic acid vapors.

Table III.B.1. x-Value in Powder Exposed to Solvent Vapors				
Solvent	% Weight Increase	Time (hours)	x-value of reacted sample	x-value of original sample
Acetone	0.125 +/- 0.025	49	0.396 +/- 0.001	0.399
Hexane	0.000 +/- 0.000	49	0.3955 +/- 0.0005	0.399
Toluene	0.30 +/- 0.00	49	0.4005 +/- 0.0015	0.408
Ethanol	0.00 +/- 0.00	72	0.399 +/- 0.0005	0.399
Methanol	0.18 +/- 0.02	49	0.3965 +/- 0.0005	0.399

*III.B. 3.2 Liquid phase reactions.* The oxygen content "x" found on suspending  $\text{YBa}_2\text{Cu}_3\text{O}_{6.5+x}$  powder in various liquid media are presented in Table III.B.2. These values were determined by the single titration method in aqueous solution, X-values obtained in these experiments (after 30 minutes reaction) by the two titration method were in the range, 0.002 to 0.006. These experiments are best rationalized by assuming that the reaction between  $\text{YBa}_2\text{Cu}_3\text{O}_{6.5+x}$  powder and the different aqueous electrolyte solutions occurs only the surface of the material. It appears that the products from the reaction of  $\text{YBa}_2\text{Cu}_3\text{O}_{6.5+x}$  powder with these solutions is an insoluble film on the surface of the superconductor which protects the  $\text{YBa}_2\text{Cu}_3\text{O}_{6.5+x}$  from further reaction with the solution.

Table III.B.2. x-Value in Aqueous Solution/ $\text{YBa}_2\text{Cu}_3\text{O}_{6.5+x}$ Powder Suspensions.		
Initial x-value of unreacted $\text{YBa}_2\text{Cu}_3\text{O}_{6.5+x}$ was 0.405.		
Solution	Reaction Time (minutes)	x-value of reacted sample
Deionized Water	10	0.3855 +/- 0.0005
Deionized Water	30	0.365 +/- 0.001
1 M NaCl	10	0.386 +/- 0.001
1 M KCl	30	0.365 +/- 0.001
1 M $\text{KNO}_3$	30	0.365 +/- 0.001
1 M NaBr	30	0.370 +/- 0.001

The reaction of  $\text{YBa}_2\text{Cu}_3\text{O}_{6.5+x}$  powder with liquid glacial acetic acid is much faster than with the vapors. In another experiment 6 drops of the liquid glacial acetic acid were added to a 0.2 g  $\text{YBa}_2\text{Cu}_3\text{O}_{6.5+x}$

sample, and the mixture thing was stored for 1 hour in a desiccator containing concentrated sulfuric acid. The x-value was found to 0.081. The reaction with liquid glacial acetic acid is very fast.  $\text{YBa}_2\text{Cu}_3\text{O}_{6.5+x}$  powder decomposes and the blue color appears. Plotting the x-value vs. % weight increases, as in Figure B.2, shows that the two are linearly correlated. Figure III.B.3 is a plot of x-value as a function of the square root of time. The line in Figure B.3, obtained for the samples exposed to concentrated ammonium hydroxide, is linear which suggests that the reaction  $\text{YBa}_2\text{Cu}_3\text{O}_{6.5+x}$  powder with ammonium hydroxide vapors is diffusion controlled.

#### III.B. 4. Conclusions

When powdered  $\text{YBa}_2\text{Cu}_3\text{O}_{6.5+x}$  reacts with vapors originating from glacial acetic acid, or concentrated aqueous ammonia, there is an increase in total weight accompanied by a decrease in the oxygen content. The decrease in oxygen content is linearly related to the increase in weight. The rate of reaction with glacial acetic vapors is much more rapid than with ammonium hydroxide vapors. The reaction with ammonium hydroxide vapors is diffusion controlled. No detectible reaction occurs in the gas phase between  $\text{Ba}_2\text{Cu}_3\text{O}_{6.5+x}$  powders and acetone, methanol, ethanol, toluene, or hexane. Exposing  $\text{YBa}_2\text{Cu}_3\text{O}_{6.5+x}$  to gaseous species and monitoring the accompanying weight change and oxygen content is a simple, reproducible method for studying the reactivity of  $\text{YBa}_2\text{Cu}_3\text{O}_{6.5+x}$  under standardized conditions.

The reaction of  $\text{YBa}_2\text{Cu}_3\text{O}_{6.5+x}$  powders with pure water and aqueous 1 M solutions of potassium chloride, potassium nitrate, sodium chloride, or sodium bromide is limited to the surface of the powder particle where a insoluble film forms which inhibits further reaction.

#### III.B.5. References

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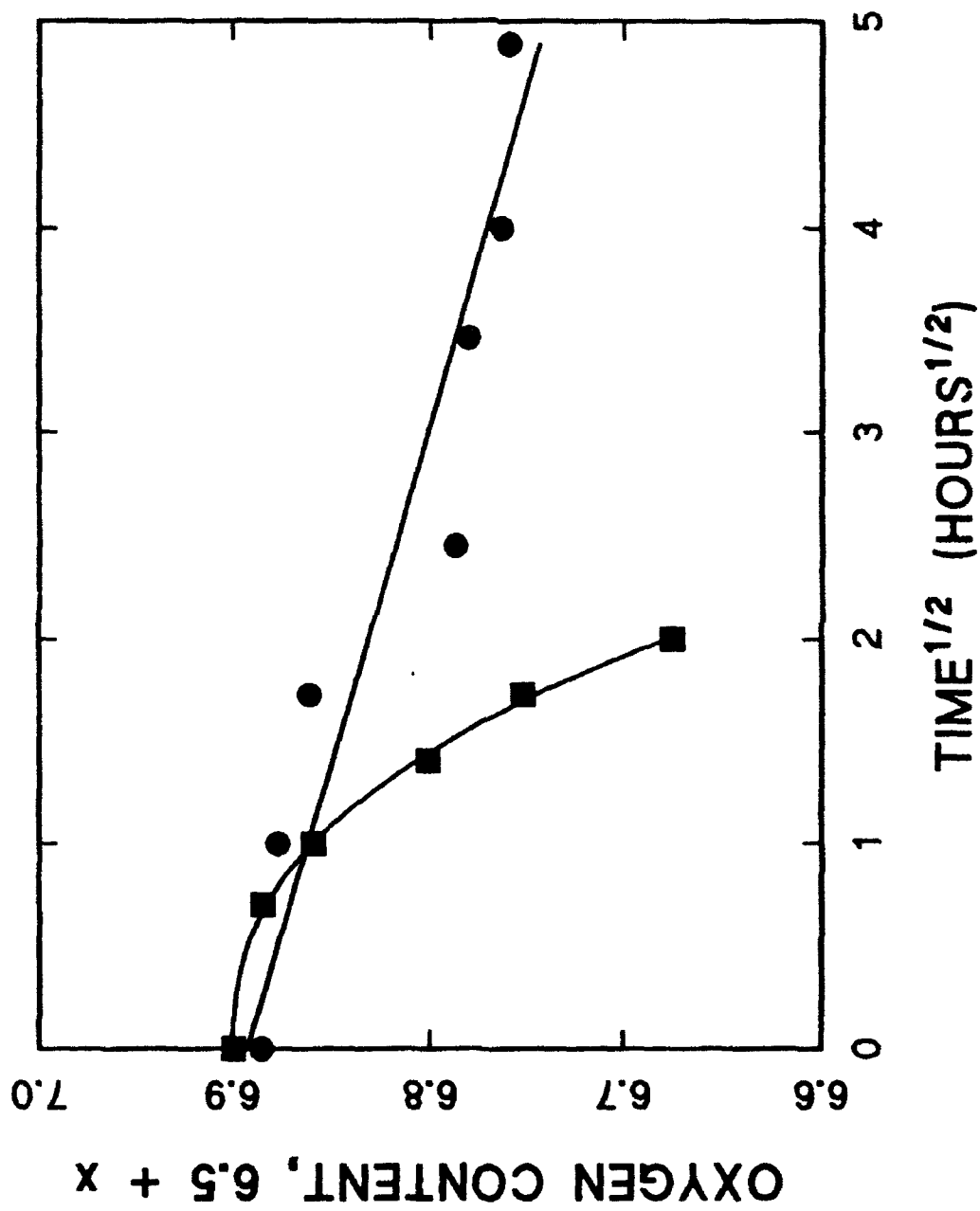


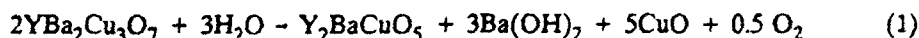
Figure B.3. X—values as a function of the square root of time in: ●— concentrated ammonium hydroxide vapors, ■— glacial acetic acid vapors.

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### III.C. Effect of Carbon Dioxide on the Reaction of $\text{YBa}_2\text{Cu}_3\text{O}_{6.5+x}$ with Water Vapor

#### III.C.1. Introduction

Since the discovery of high temperature yttrium-based superconducting oxide<sup>1</sup> over a dozen or so papers have been published on the effect of moisture on the properties of these materials<sup>2-12</sup>. Some of the reported results are in disagreement. The superconductivity of  $\text{YBa}_2\text{Cu}_3\text{O}_{6.5+x}$  samples is greatly degraded by interaction with water and humid air. In particular, the superconductive orthorhombic  $\text{YBa}_2\text{Cu}_3\text{O}_7$  phase reacts with water and evolves oxygen. The following reactions may be expected<sup>2</sup>



Barkatt, et. al.<sup>12</sup> have reported the leaching of  $\text{YBa}_2\text{Cu}_3\text{O}_{6.5+x}$  to be a highly incongruent process. Gallagher et. al.<sup>9</sup> have concluded that when  $x$  in  $\text{YBa}_2\text{Cu}_3\text{O}_{6.5+x}$  goes from  $-0.5$  to  $+0.5$  the superconducting orthorhombic phase undergoes a transition to the non-superconducting tetragonal phase at  $\text{O}_{6.63}$ . Harris, et. al.<sup>8</sup> report loss of superconductivity and an associated phase change, orthorhombic-tetragonal, on exposure to moisture.

Harris, et. al. saw the phase change occurring in a sample that had been pressed into a pellet, sintered and annealed in oxygen for 1 hour at  $550^\circ\text{C}$ , the resulting oxygen stoichiometry being determined to be  $\text{O}_{6.6}$ . A second sample which was annealed for 32 hours at  $550^\circ\text{C}$  had an oxygen stoichiometry approaching  $\text{O}_7$ , and did not exhibit the phase change on exposure to moisture. This apparently can occur when oxygen stoichiometry approaches the lower range of that identified as orthorhombic.

The aim of the present work is to study the reaction of superconducting  $\text{YBa}_2\text{Cu}_3\text{O}_{6.5+x}$  powder with saturated water vapor in the presence of  $\text{CO}_2$ , in the absence of  $\text{CO}_2$ , and in dry  $\text{CO}_2$ . The samples were exposed to:

- 1)  $\text{CO}_2$  saturated water vapor atmosphere.
- 2) Ambient water vapor atmosphere (contains  $\sim 0.033\%$   $\text{CO}_2$ ).
- 3)  $\text{CO}_2$ -free water vapor atmosphere.
- 4) Pure, dry  $\text{CO}_2$  (1 atm.)

#### III.C.2. Experimental

Powder samples (0.2 g) on watchglasses or in XRD sample holders were placed in desiccators containing either carbonated water, deionized water, or 1 M sodium hydroxide. The samples were exposed to these atmospheres for times in the range from 1 hour to 5 days. All samples were weighed before and after

exposure to these atmospheres. Samples were also placed in dry carbon dioxide (1 atm) with weight changes determined over a 25 hour period. The iodometric titration method was used to determine the oxygen content  $(6.5 + x)$  of  $\text{YBa}_2\text{Cu}_3\text{O}_{6.5+x}$  powder before and after exposure to 1 M sodium hydroxide ( $\text{CO}_2$  free water vapor).

**2.1. Titration by Iodide method.** The sample was placed into a flask containing 100 ml of oxygen-free 0.33 M hydrochloric acid and 7.76 g of potassium iodide. The stoppered erlenmeyer flask was placed in an ultrasonic bath for several minutes to dissolve the sample and then immediately was titrated with standardized 0.1 M sodium thiosulfate using 4 ml of 0.2% starch solution as an indicator. The value of  $x$  was calculated from the relation:

$$x = [658.22 \times M \times V - 3g] / [2g - 16 M \times V] \quad (3)$$

The value of  $x$  was calculated from the weight of sample taken (g-grams), the volume of thiosulfate required to reach the endpoint (V-liters) and the molarity of the thiosulfate (M).

### III.C3. Results and Discussion

The results of reacting  $\text{YBa}_2\text{Cu}_3\text{O}_{6.5+x}$  powder with saturated water vapor, both  $\text{CO}_2$ -free and in the presence of two levels of  $\text{CO}_2$ , are presented in Figures C.1 and C.2. The samples exposed to the saturated water vapor free of  $\text{CO}_2$  gained about 43 weight % after exposure for 24 hours (Figure C.1). The samples exposed to the ambient water vapor atmosphere (0.033%  $\text{CO}_2$ ) steadily gained weight over a 25 hour period, attaining a final weight gain of 33.3%. Significantly, the samples exposed to a water vapor atmosphere saturated with  $\text{CO}_2$  gained a only total of about 3 wt % even after exposure for 24 hours. Remarkably, in the absence of water vapor, carbon dioxide produces a negligible weight change. Accordingly, the reaction of  $\text{CO}_2$  with  $\text{YBa}_2\text{Cu}_3\text{O}_{6.5+x}$  requires the presence of water.

Plotting the oxygen content  $(6.5 + x)$  vs % weight increase, as in Figure C.2, shows that the two are linearly correlated.

X-ray diffraction experiments were undertaken to identify, as a function of time, the phases present in  $\text{YBa}_2\text{Cu}_3\text{O}_{6.5+x}$  during its reaction with water vapor and  $\text{CO}_2$ . XRD spectra were obtained over regular time intervals for as long as 26 days. Initially we will discuss the behavior over the first 24-25 hours. For brevity, XRD spectra are given only for the 24-25 hour experiments. Figure C.3 summarizes these results obtained after exposure of  $\text{YBa}_2\text{Cu}_3\text{O}_{6.5+x}$  to various water/ $\text{CO}_2$  atmospheres after 24-25 hours. These X-ray data confirm that  $\text{CO}_2$  drastically influences the degradation of  $\text{YBa}_2\text{Cu}_3\text{O}_{6.5+x}$  powder upon exposure to water vapor.

In the presence of 1 atm  $\text{CO}_2$  + saturated water vapor, very little degradation of the  $\text{YBa}_2\text{Cu}_3\text{O}_{6.5+x}$  powder is seen (See Figures C.3 and C.4). The only reaction products detected are a  $\text{BaCO}_3$  (the primary one) and a small amount of  $\text{CuO}$ .

In the presence of atmospheric levels of  $\text{CO}_2$  the initial reaction product observed at short times is  $\text{Ba(OH)}_2$ . At longer times  $\text{Ba(OH)}_2$  is converted to  $\text{BaCO}_3$  by reaction with the 0.033%  $\text{CO}_2$  in the atmosphere. The two major phases are  $\text{Ba(OH)}_2$  and  $\text{BaCO}_3$  after one day. There is some evidence of the formation of  $\text{Y(OH)}_3$  and  $\text{Cu(OH)}_2$ , along with  $\text{BaCuO}_2$ ,  $\text{Y}_2\text{BaCuO}_5$  and  $\text{CuO}$  as other decomposition products.

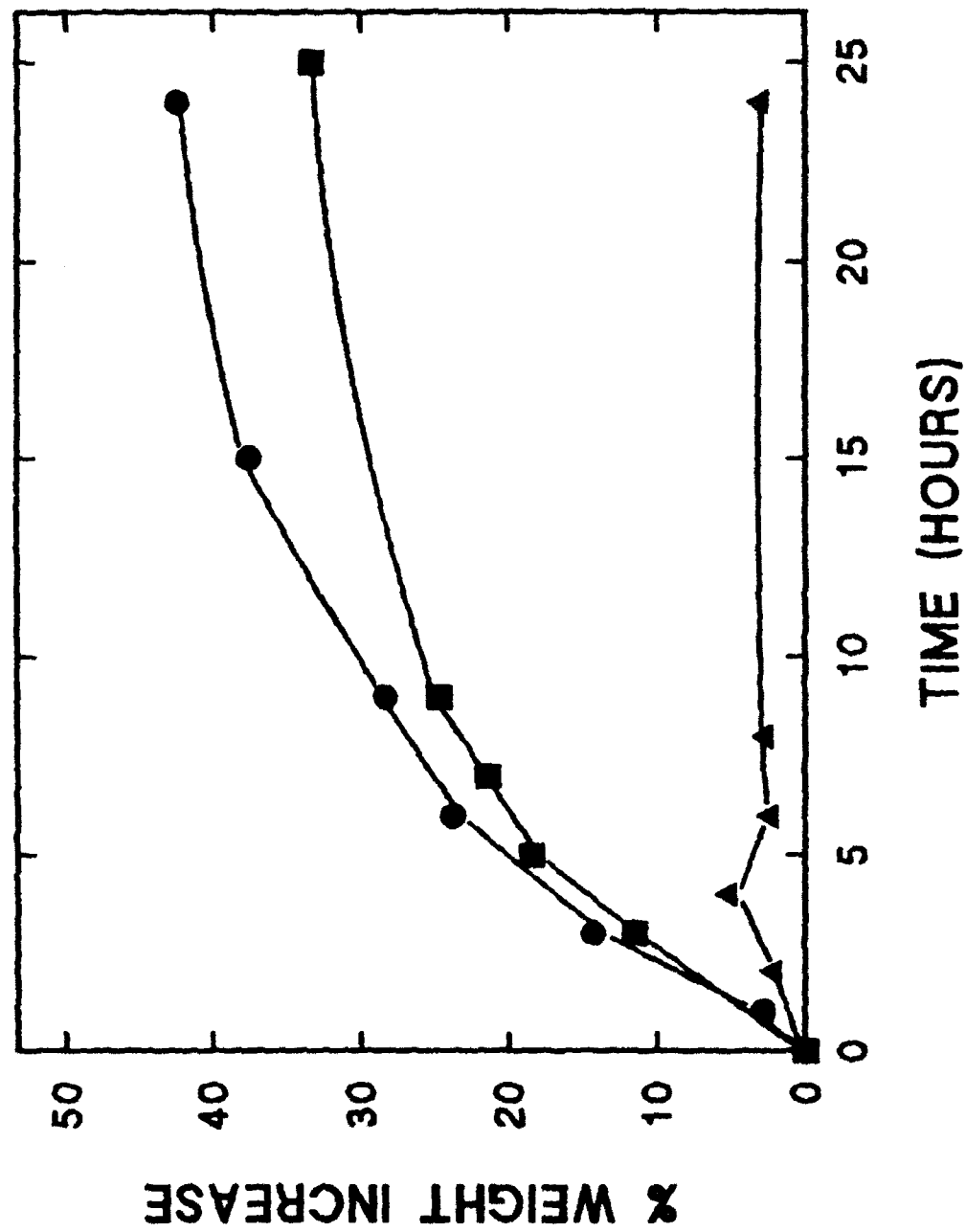


Figure C.1. Weight gain vs time. The samples were exposed to: ● — CO<sub>2</sub> free water vapor atmosphere, ■ — ambient water vapor atmosphere and ▲ — CO<sub>2</sub> saturated water vapor atmosphere.



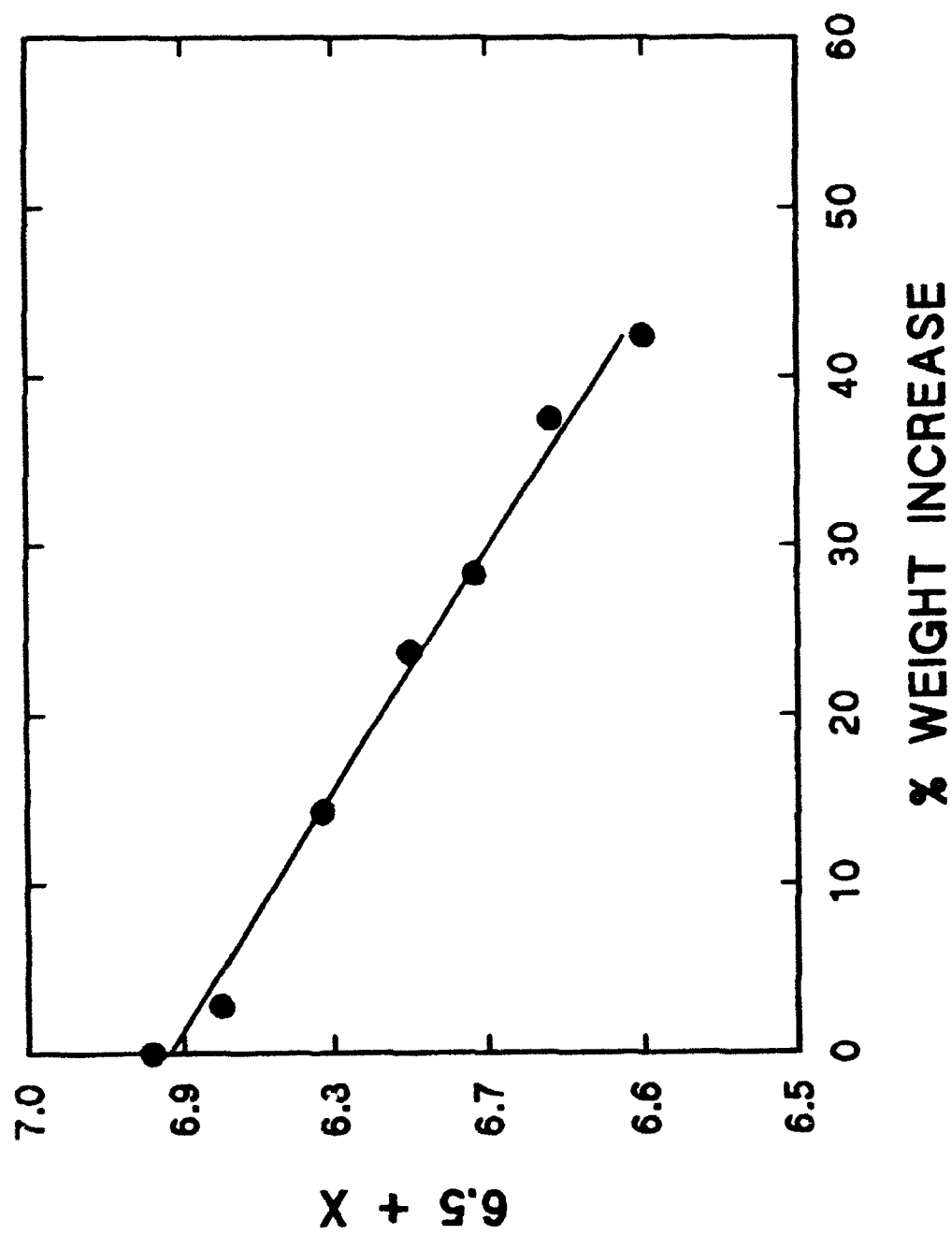


Figure C.2. Relationship between sample weight and oxygen decrease. The samples were exposed to CO<sub>2</sub> free water vapor atmosphere.

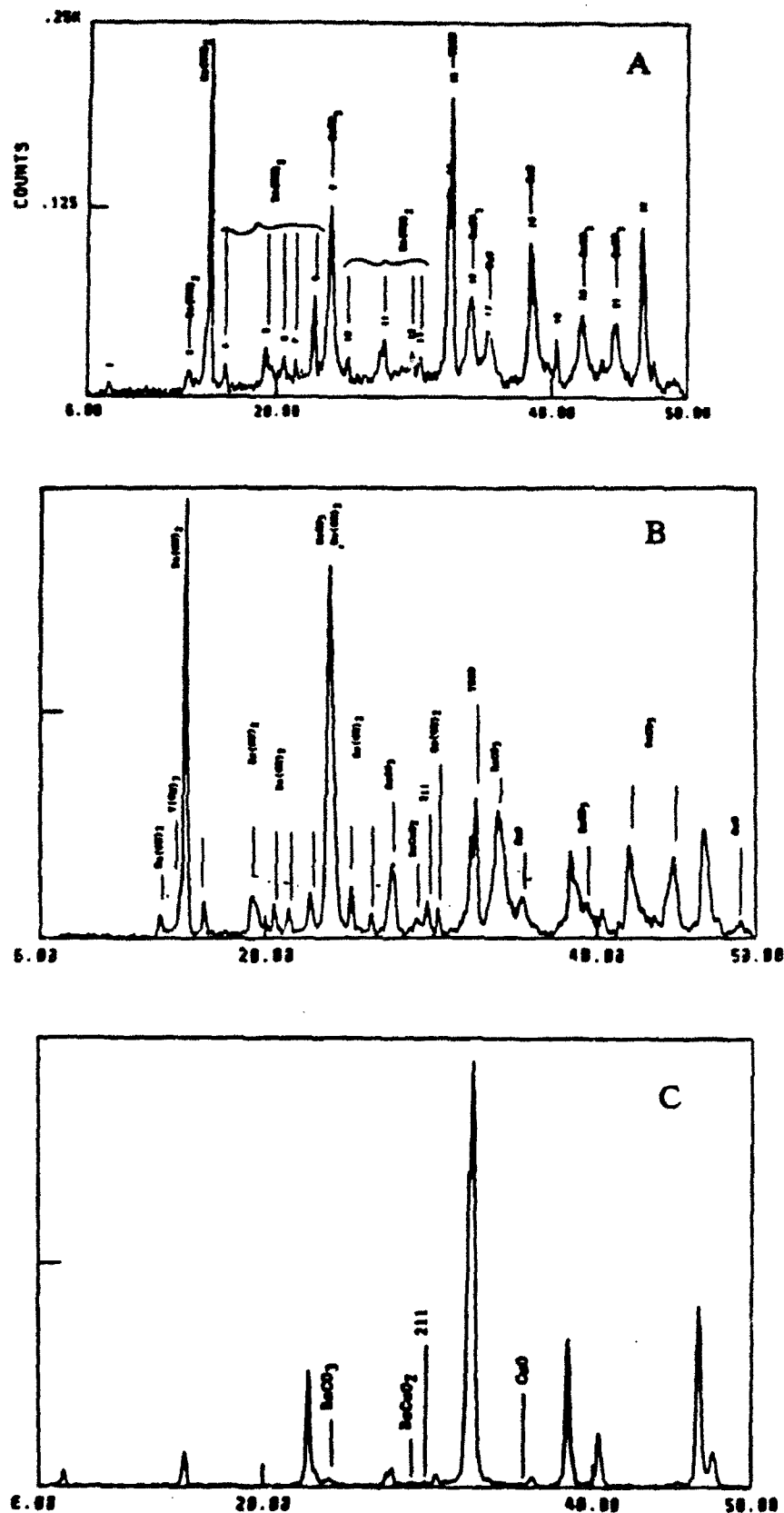


Figure C.3. XRD patterns after 24-25 hours exposure of  $\text{YBa}_2\text{Cu}_3\text{O}_{6.5+x}$  sample to: a)  $\text{CO}_2$  free-24 hours; b) ambient-25 hours; c) pure  $\text{CO}_2$  in saturated water vapor atmosphere-24 hours. Patterns were run from 6 to 50 degrees  $2\theta$ .

The effect of  $\text{CO}_2$ -free water vapor is much more dramatic than that found in the presence of atmospheric levels of  $\text{CO}_2$ .  $\text{Ba(OH)}_2$  starts to appear after only two hours exposure along with  $\text{BaCO}_3$  and  $\text{CuO}$ . After 24-25 hours exposure  $\text{Ba(OH)}_2$  is the major phase seen with  $\text{YBa}_2\text{Cu}_3\text{O}_{6.5+x}$ ,  $\text{BaCO}_3$ , and  $\text{CuO}$  occurring as secondary phases. Neither  $\text{Y(OH)}_3$  nor  $\text{Cu(OH)}_2$  were observed although it is possible that they are present as amorphous phases. Yan et al.<sup>2</sup> found evidence of an amorphous surface layer with some indication of the presence of  $\text{Cu(OH)}_2$ . Troler et al. report data supporting the presence of  $\text{Y(OH)}_3$ <sup>11</sup> while Bansal and Sandkuhl found no reaction products containing Y.<sup>7</sup> After 4 days in the desiccator all of the  $\text{Ba(OH)}_2$  had converted into  $\text{BaCO}_3$ , that being the primary phase present along with  $\text{YBa}_2\text{Cu}_3\text{O}_{6.5+x}$ ,  $\text{Y}_2\text{BaCuO}_5$ , and  $\text{CuO}$ . The formation of  $\text{BaCO}_3$  is the result of unavoidable exposure of the sample to  $\text{CO}_2$  in the atmosphere during the XRD measurements. These same reaction products were reported by Yan et al.<sup>2</sup> After 11 days in the desiccator, the X-ray pattern was essentially the same as the 4 day result.

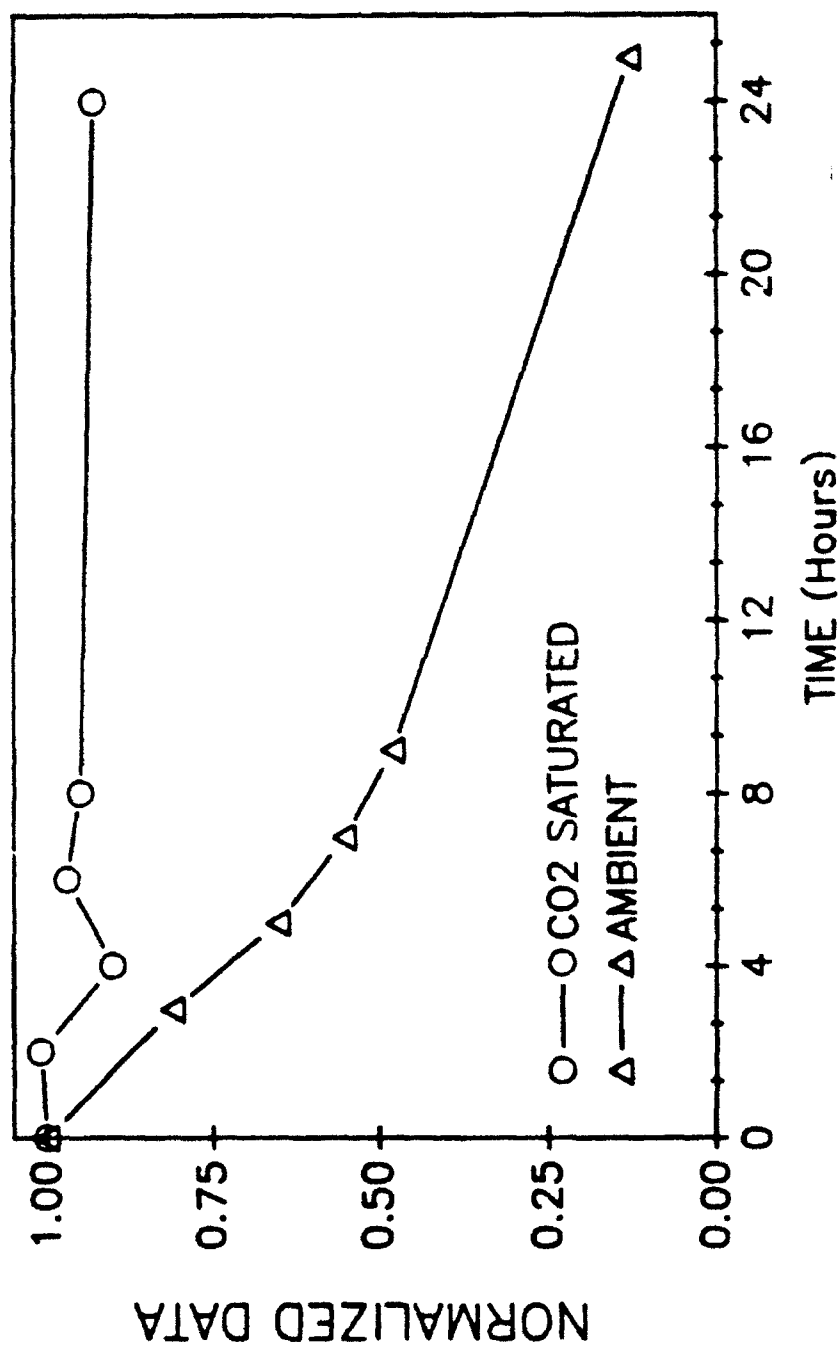
Overall the sample gained approximately 53 wt % while stored in the wet atmosphere, and subsequently lost approximately 24 wt % while stored in a desiccator. None of our data (Figure C.5) show evidence of the phase change orthorhombic-tetragonal. The intensity ratios of the 200 to 020  $\text{YBa}_2\text{Cu}_3\text{O}_{6.5+x}$  peaks are essentially unchanged with time on exposure to water vapor, thus indicating that orthorhombic  $\text{YBa}_2\text{Cu}_3\text{O}_{6.5+x}$  degrades directly to the decomposition products without going through an intermediate tetragonal phase change which then decomposes.

Figure C.6 is a plot of the normalized X-ray intensity and X values as a function of time. The maximum number of counts at the 103/110  $\text{YBa}_2\text{Cu}_3\text{O}_{6.5+x}$  peak was normalized. The two curves represented in Figure C.6 practically superimpose. Consequently the value of "X" as measured by titration and XRD is essentially the same.

Figure C.7 is a plot of the normalized X-ray intensity and X values as a function of the *square root* of time. The two lines in Figure C.7 are practically linear which suggests that the reaction of  $\text{YBa}_2\text{Cu}_3\text{O}_{6.5+x}$  powder with water vapor is diffusion controlled. This has been shown previously in the literature<sup>6</sup>. The differences in degree of reaction between the  $\text{CO}_2$  saturated, ambient and  $\text{CO}_2$  free water vapor environments are striking. The presence of a high concentration of  $\text{CO}_2$  causes the formation of an impervious surface reaction product ( $\text{BaCO}_3$ ) which then protects the underlying  $\text{YBa}_2\text{Cu}_3\text{O}_{6.5+x}$  from continued decomposition. This idea is supported by the weight change data as seen in Figure C.1. The data for samples exposed to the  $\text{CO}_2$  saturated atmosphere shows hardly any change in the intensity of the 103/110  $\text{YBa}_2\text{Cu}_3\text{O}_{6.5+x}$  peak after 24 hours exposure while the samples exposed to the ambient atmosphere show a continuous decrease in the intensity of this peak (See also Figure C.4).

### III.C.4. Conclusions

The rate of reaction of  $\text{YBa}_2\text{Cu}_3\text{O}_{6.5+x}$  with water vapor is decreased by the presence of  $\text{CO}_2$ . The initial reaction product between the superconductor and water is  $\text{Ba(OH)}_2$ . The decreased rate of reaction is caused by the formation of a thin, protective overlayer of  $\text{BaCO}_3$  produced by reaction of  $\text{Ba(OH)}_2$  with  $\text{CO}_2$ . There is no evidence for a significant, direct reaction of  $\text{YBa}_2\text{Cu}_3\text{O}_{6.5+x}$  with dry  $\text{CO}_2$ .



**Figure C.4.** Normalized X-Ray intensity as a function of time for 103/110  $\text{YBa}_2\text{Cu}_3\text{O}_{6.5+x}$  peak.  $\text{YBa}_2\text{Cu}_3\text{O}_{6.5+x}$  exposed to water vapor containing ambient level  $\text{CO}_2$  or 1 atmosphere of  $\text{CO}_2$ . Values normalized to their values at zero time.

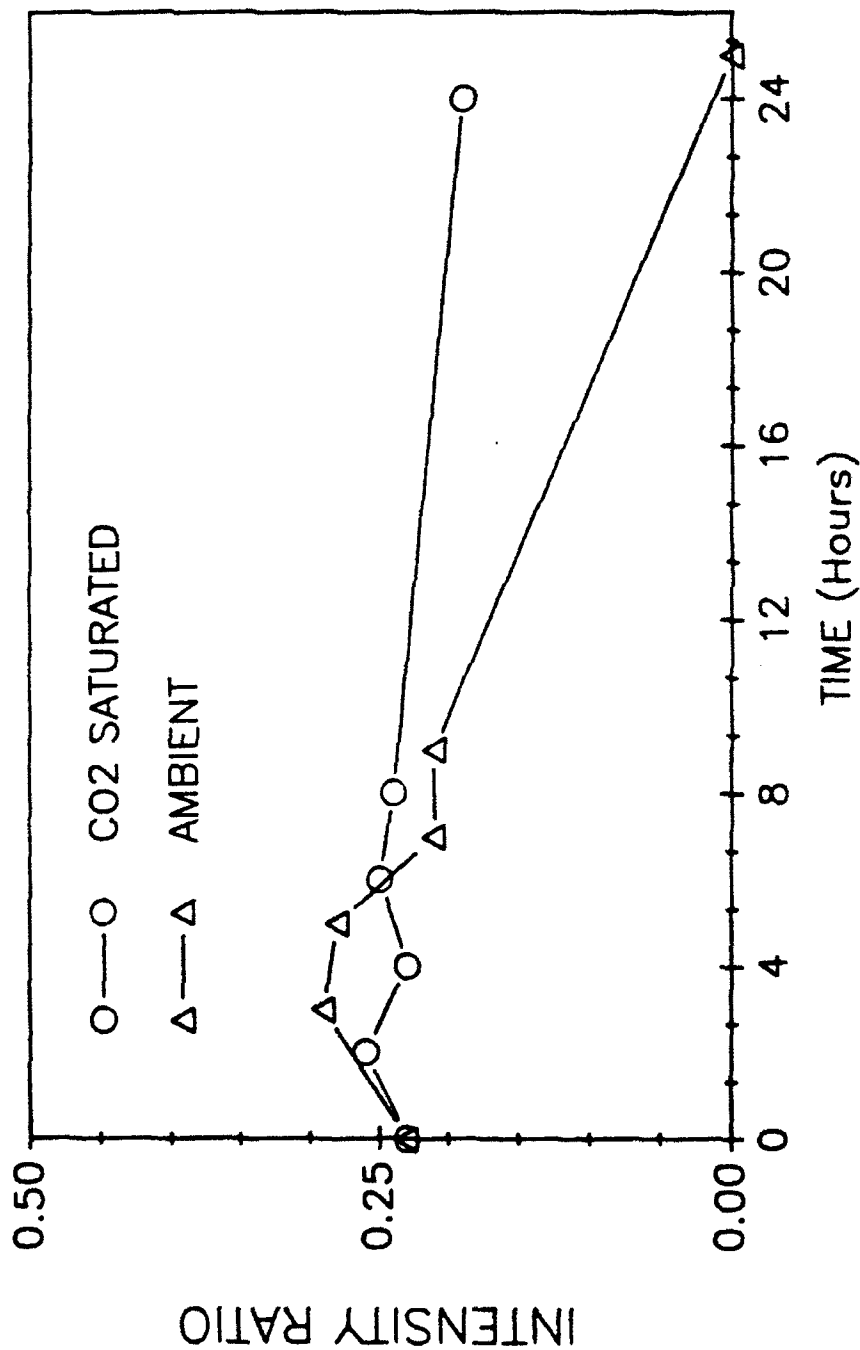


Figure C.5. Intensity Ratio of the 200 and 020  $\text{YBa}_2\text{Cu}_3\text{O}_{6.5+x}$  peaks.  $\text{YBa}_2\text{Cu}_3\text{O}_{6.5+x}$  exposed to water vapor containing ambient level  $\text{CO}_2$  or 1 atmosphere of  $\text{CO}_2$ . Ambient level datum at 25 hours is unreliable as the split between the two peaks could not be resolved.

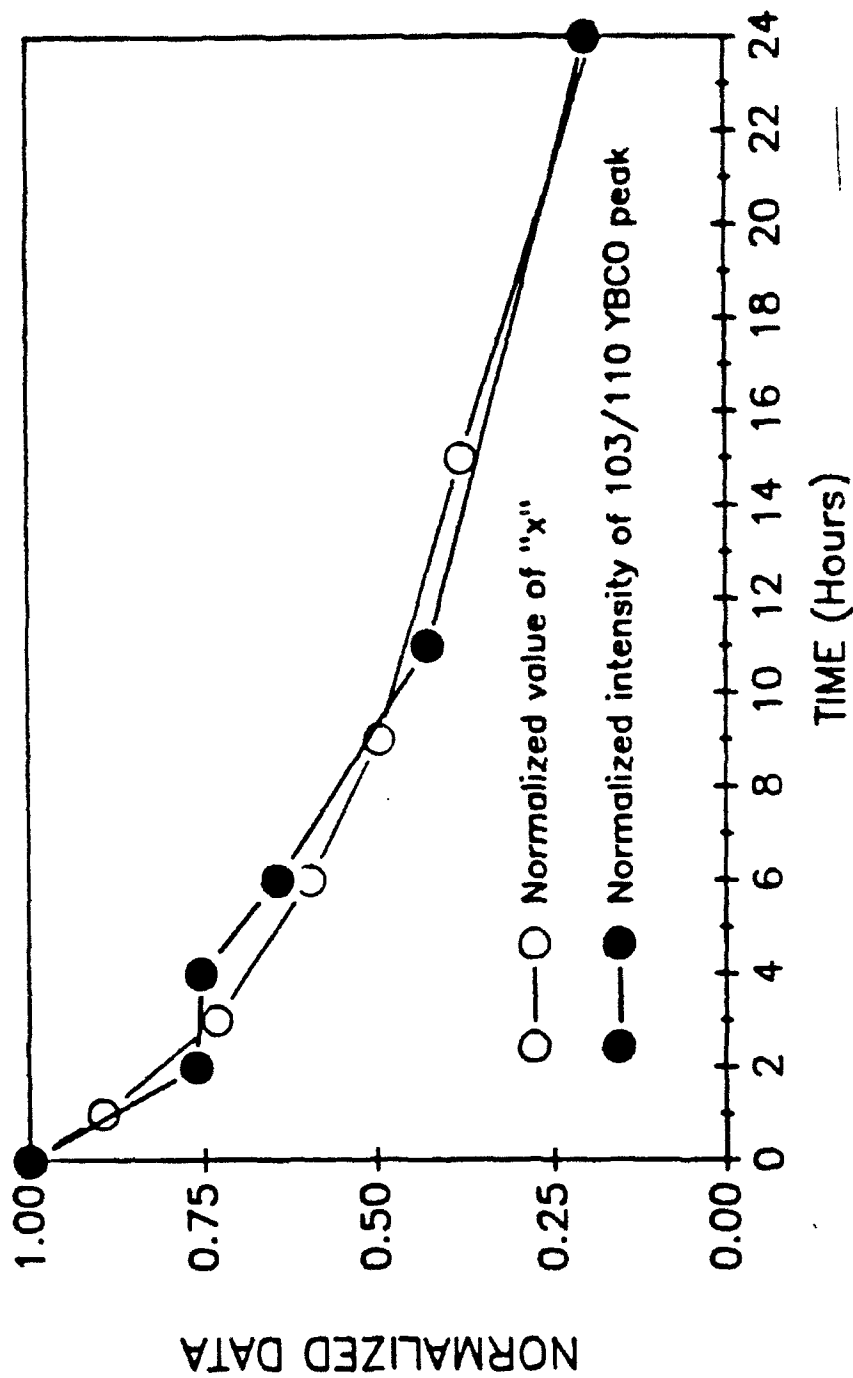
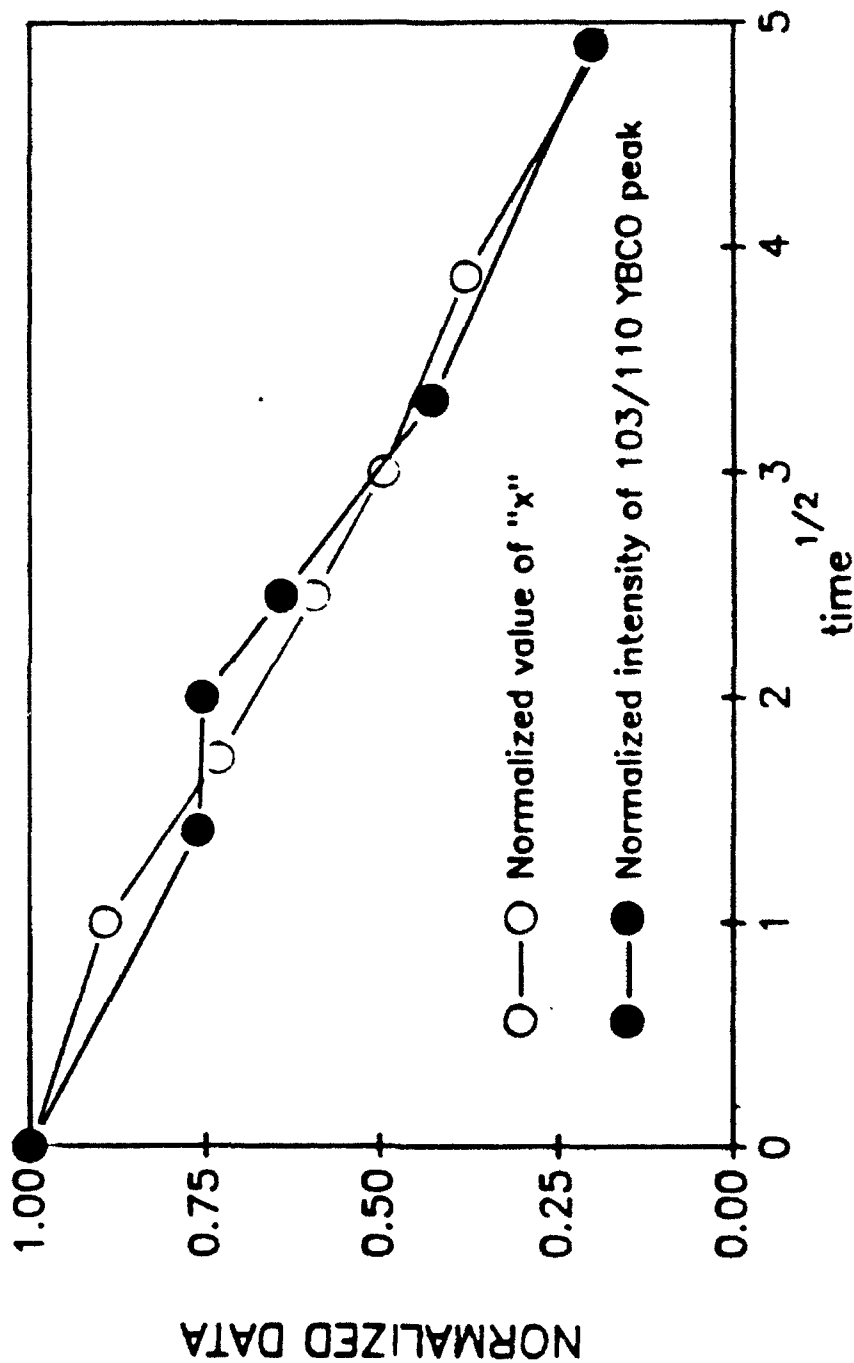


Figure C.6. Normalized X-Ray intensity and measured "X" value as a function of time in CO<sub>2</sub>-free water vapor. Both values normalized to their values at zero time. 103/110 YBa<sub>2</sub>Cu<sub>3</sub>O<sub>6.5+x</sub> peak.



**Figure C.7.** X-ray intensity and measured "X" value as a function of the square root of time in  $\text{CO}_2$  free water vapor. Both values normalized to their values at zero time. 103/110  $\text{YBa}_2\text{Cu}_3\text{O}_{6.5+x}$  peak.

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### III.D. DETERMINATION OF OXYGEN CONTENT IN $\text{YBa}_2\text{Cu}_3\text{O}_{6.5+x}$

#### III.D.1. Introduction

With the discovery of high temperature superconductors [1],[2], the problem of the determination of oxygen content in  $\text{YBa}_2\text{Cu}_3\text{O}_{6.5+x}$  ( $\text{YBaCuO}$ ) became important. This material is superconducting in the range ca.  $0 < x < 0.5$ . Various analytical methods have been used to determine  $x$  [3],[4],[5],[6],[7],[8],[9] and a simple iodometric method [14] appeared to be the most reliable and convenient. It involves dissolving the  $\text{YBaCuO}$  in 0.35 M hydrochloric acid containing iodide ion under oxygen-free conditions. Iodine is produced by reactions whose stoichiometry is determined by:

- 1) oxygen contents in excess of 6.5. It is unnecessary to assume that  $\text{Cu(III)}$  exists in the superconducting form of  $\text{YBaCuO}$  in order to calculate  $x$ . Conventional stoichiometric methods based on overall balanced equations suffice. However, we, as others do, shall use the nomenclature that assumes the existence of  $\text{Cu(III)}$  for convenience, and
- 2) the classical reaction of cupric species with iodide ion to make iodine and insoluble  $\text{CuI}$ .

The iodine is titrated with sodium thiosulfate as the titrant using starch as the indicator. Then another sample of  $\text{YBaCuO}$  is dissolved in oxygen-free hydrochloric acid which does not contain iodide ion, and allowed to stand. This simple procedure makes  $x = 0$ . Next iodide ion is added, and the iodine produced by the



reaction with copper (II) in solution is determined by titration with thiosulfate. The difference in the quantity of sodium thiosulfate consumed in these two titrations yields the value of  $x$ . This method has some shortcomings since iodide ions may be oxidized by atmospheric oxygen, a reaction that is catalyzed by Cu(I). Consequently, purging of solutions with an inert gas is necessary. Also it requires two titrations, doubling the effort. In addition, while the dissolution of finely powdered YBaCuO is rapid in the hydrochloric acid mixture, the dissolution of sintered, bulk forms of YBaCuO is slow, taking from hours to days depending on the size and density of the YBaCuO sample. Frequently, we found when analyzing dense, bulk samples that the resulting values of  $x$  were erroneously high.

The aim of the present work is to describe a new analytical method which allows the determination of the value of  $x$  in  $\text{YBa}_2\text{Cu}_3\text{O}_{6.5+x}$ . This procedure is not subject to the above mentioned complications. It involves the dissolution technique for YBaCuO described by Appelman et al. [11]. They dissolved YBaCuO in ice - cold 4.4 M HBr to produce bromine in an amount directly related to the value of  $x$ . The bromine was then converted to iodine by subsequent reaction with iodide ion dissolved in ammonia to produce a precipitate of CuI in slightly acid solution. Sodium citrate was then added to redissolve the CuI. The citrate complexes causes CuI to react with an equivalent amount of  $\text{I}_2$  to produce a citrate complex of Cu(II) and iodide ion. Thus in the subsequent titration with sodium thiosulfate only iodine corresponding to the value of  $x$  should be found. We established that dissolution of bulk, sintered forms of YBaCuO was very rapid in the HBr solution and confirmed that the remainder of the Appelman et. al. procedure yields reproducible results.

In order to provide a new means of determining the value of  $x$  by a non-iodometric method, we elected to determine the bromine produced on dissolving YBaCuO in HBr by using excess As(III) and back titrating with potassium bromate. This is a classical procedure [10], [11] for determination of As(III) in acid solutions containing bromide ion. This report describes conditions that allow the As(III) method to be performed in a manner insensitive to atmospheric oxygen and usable with 0.5 to 200 milligram amounts of YBaCuO. Special problems were found to exist with the bromate method when Cu(II) is present in strong HBr solutions.

### III.D.2. Experimental

#### III.D.2.1. Hydrobromic Acid Dissolution Methods.

*III.D.2.1.1. Procedure 1.* Ice-cold 4.4 M solution of HBr containing an known amount of As(III), 0.252 mmol, was added to a 50 - 200 mg sample of YBaCuO in a vial having a Teflon-lined screw cap. One ml of HBr solution was used for every 20 mg of YBaCuO. This vial was held at room temperature, shaken occasionally, and dissolution of YBaCuO occurred in 10-30 minutes. The contents of the vial were transferred to 90 ml of 1.2 M HCl and mixed. The unreacted As(III) was determined by back titration with 0.002 M potassium bromate solution by potentiometric titration using a platinum indicator electrode and a saturated calomel reference.

*III.D.2.1.1. Procedure 2.* An ice-cold, 4.4 M solution of HBr was added to a 50 - 200 mg sample of YBaCuO in a vial with a Teflon-lined screw cap. One ml of HBr solution was used for every 20 mg of YBaCuO. This vial was held at room temperature, shaken occasionally, and dissolution of YBaCuO occurred in a 10-30 minutes, producing a bromine solution containing Cu(II). The bromine/Cu(II)-containing solution was transferred to 100 ml of 1.2 M solution of HCl. The vial and pipet used in this procedure were washed with 1 M potassium bromide. Then 5 ml of 0.0504 M As(III) was added. The excess As(III) was titrated with 0.002 M potassium

bromate solution. The endpoint was detected potentiometrically using a Pt reference electrode and a SCE reference electrode.

### III.D.3. Results and Discussion

Our goal was to determine the value of  $x$  in dense, sintered samples of  $\text{YBaCuO}$  weighing as little as a few milligrams. Our starting premise was that the method should be rapid, not involve expensive or complicated equipment and be simple enough that relatively unskilled personnel could perform it under ordinary laboratory conditions. Furthermore, the method should not be sensitive to the presence of oxygen and should have a sufficiently low blank to permit the accurate determination of  $x$  in sample weights in the low milligram range. Volumetric titrations meet this general requirement. Consequently we sought a volumetric method which would only consume titrant for  $\text{YBa}_2\text{Cu}_3\text{O}_{6.5+x}$  samples whose stoichiometry was in the range  $0 < x < 0.5$ . Such a method should not respond to the total copper content of  $\text{YBaCuO}$  in order to avoid errors caused by trace phases of other copper containing compounds.

We used a combination of two literature methods. The dissolution of  $\text{YBa}_2\text{Cu}_3\text{O}_{6.5+x}$  was carried out in cold 4.4 M  $\text{HBr}$  according to Appelman et al. [3] to produce  $\text{Br}_2$  in a stoichiometric amount directly related to  $x$ . Then, after diluting in 1.2 M  $\text{HCl}$ ,  $\text{As(III)}$  in excess of the amount required for the bromine was added, and this unreacted  $\text{As(III)}$  was determined using potassium bromate and a potentiometric endpoint. We established the conditions for performing this classical bromate titration [10], [11] that it were insensitive to oxygen and suitable for milligram levels of superconductor.

Figure D.1 shows the potentiometric titration curves for the specified procedures. Substantial potential changes occur at the endpoint. Procedure 1 yields impossibly high results because the air oxidation of  $\text{As(III)}$  is catalyzed in 4.4 M  $\text{HBr}$ . Oxygen is not a problem if the dissolution mixture is diluted with 1.2 M  $\text{HCl}$  before adding the  $\text{As(III)}$ , as is done in Procedure 2. Procedure 2 was used for all further analyses.

Figure D.2 summarizes nine titrations of milligram amounts  $\text{YBa}_2\text{Cu}_3\text{O}_{6.5+x}$  in fiber form (these fibers were used in several of the previous sections). It is a plot of the volume of  $\text{As(III)}$  consumed (Volume,  $V$ ) vs fiber weight (Weight,  $M$ ). The least squares equation is  $V = -0.0043$  (std. dev. = 0.0081) + 0.0781 (std. dev. = 0.0052)  $M$ . The intercept is not significantly different from zero.

Powder samples of  $\text{YBa}_2\text{Cu}_3\text{O}_{6.5+x}$  weighing between 0.5 to 7.5 mg were also analyzed with equally satisfactory results [12].

### III.D.4. Conclusions

1. A new method for the determination of the  $x$ -value in  $\text{YBa}_2\text{Cu}_3\text{O}_{6.5+x}$  was developed. This method was used for  $\text{YBaCuO}$  powders and fibers. The procedure involves dissolving the  $\text{YBaCuO}$  in 4.4 M  $\text{HBr}$  to produce bromine. If the solution is first diluted ten times with 1.2 M  $\text{HCl}$  before adding excess  $\text{As(III)}$ , the bromine then reacts quantitatively with  $\text{As(III)}$ . The excess  $\text{As(III)}$  can then be titrated with potassium bromate. As long as the specified order of reagent addition is followed, the bromine/arsenic method is not oxygen sensitive.
2. Analysis of milligram - range samples gave results indistinguishable from those for larger (ca. 50 - 200 mg) ones.
3. Sub-milligram amounts of  $\text{YBaCuO}$  probably could be determined by the bromine/arsenic method.

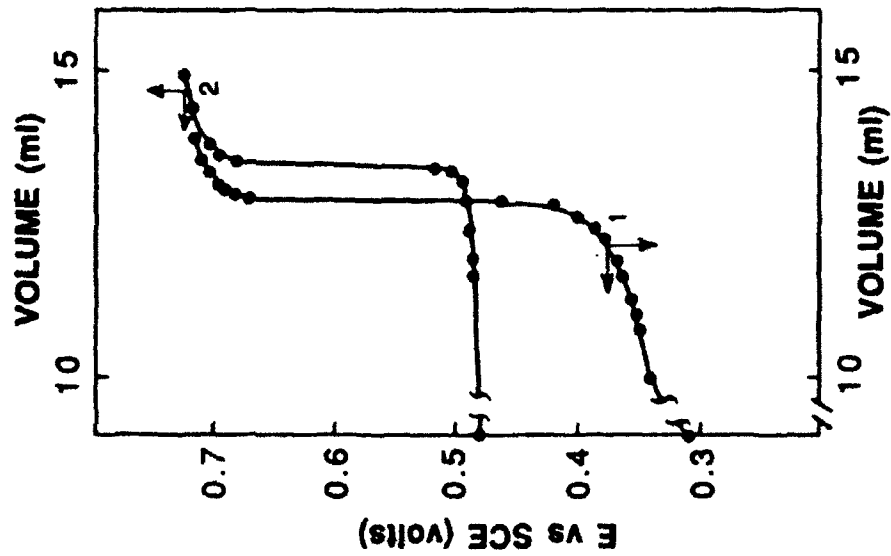


Figure D.1. Potentiometric Titrations. Curve 1 - Procedure 1, 0.1694 g YBaCuO. Curve 2 - Procedure 2, 0.1547 g YBaCuO.

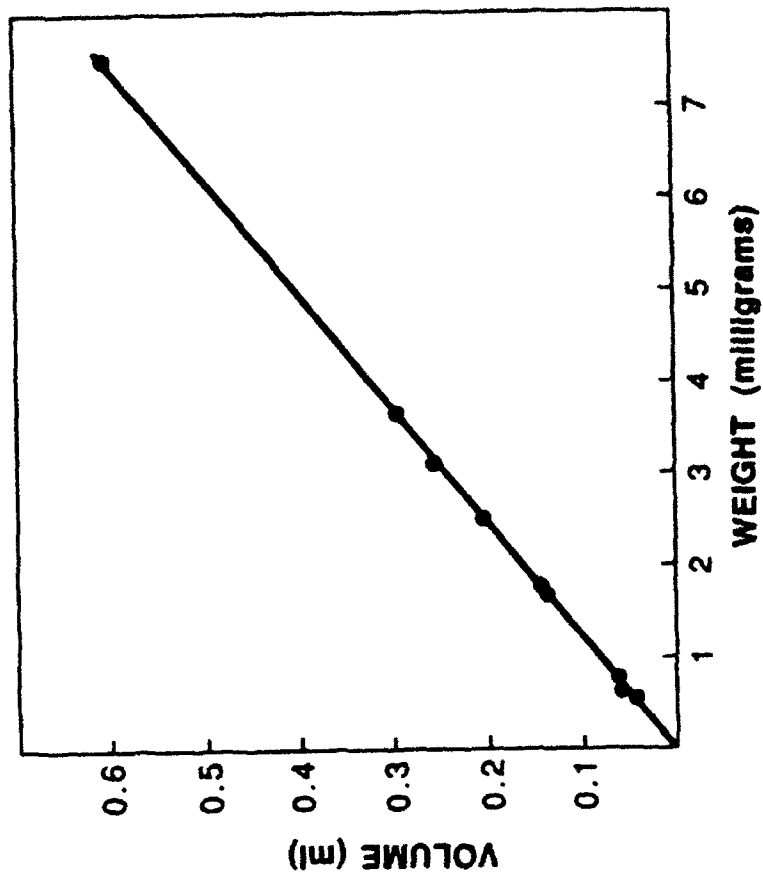


Figure D.2. Titration of milligram amounts of  $\text{YBa}_2\text{Cu}_3\text{O}_{6.88}$  fiber. Plot of end point volume, V, vs weight of superconductor fiber.

4. The precision and accuracy of the various studied techniques and the agreement between them suggest that the uncertainty in determination of the value of  $x$  in  $\text{YBaCuO}$  is on the order of 0.01 - 0.02 unit. While particular methods may yield higher internal precision, approaching 0.001 - 0.002 unit, the various volumetric methods are subject to small errors which have yet to be fully explored.

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